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CAN SUPERABSORBENT POLYMERS MITIGATE SHRINKAGE IN CEMENTITIOUS MATERIALS BLENDED WITH SUPPLEMENTARY CEMENTITIOUS MATERIALS?

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Abstract

A promising way to mitigate autogenous shrinkage in cementitious materials with a low water-to-binder ratio is internal curing by the use of superabsorbent polymers. Superabsorbent polymers are able to absorb multiple times their weight in water and can be applied as an internal water reservoir to induce internal curing and mitigation of self-desiccation. Their purposefulness has been demonstrated in Portland cement pastes with and without silica fume. Nowadays, fly ash and blast-furnace slag containing binders are also frequently used in the construction industry. The results on autogenous shrinkage in materials blended with fly ash or blast-furnace slag remain scarce, especially after one week of age. This paper focuses on the autogenous shrinkage by performing manual and automated shrinkage measurements up to one month of age. Without superabsorbent polymers, autogenous shrinkage was reduced in cement pastes with the supplementary cementitious materials versus Portland cement pastes. At later ages, the rate of autogenous shrinkage is higher due to the pozzolanic activity of the supplementary cementitious materials. Internal curing by means of superabsorbent polymers is successful, independent of this long-term higher rate of shrinkage in mixtures with supplementary cementitious materials. Superabsorbent polymers proved to be successful in mitigating self-desiccation.

1. Introduction

Autogenous shrinkage predominantly occurs in systems with a low water-to-binder ratio. Upon mixing, when cement reacts with water, hydration products will be formed in the water-filled spaces between the solid particles. As a consequence of chemical shrinkage water menisci will progressively recede in the pore structure and thus create a reduction of the internal relative humidity, i.e. self-desiccation will occur, and due to increased hydrostatic tension forces, the distance between the solid particles will be reduced, i.e. autogenous shrinkage will occur. This may result in micro- and macro-cracking, impairing the overall

strength and durability. This cracking may accelerate ingress of water or gases and in the end thereby reduce the service life of the concrete.

Autogenous shrinkage can be mitigated by supplying an external or internal water source to the hydrating system which maintains the internal relative humidity. As internal water source, several materials can be used: lightweight aggregates, pumice, expanded clay, and superabsorbent polymers (SAPs) amongst others [1, 2]. In this paper, the focus lies on SAPs. Those materials may be able to absorb e.g. 500 times their own weight in fluids and to retain it in their polymeric structure. Upon mixing, they will absorb part of the mixing water. This water is then available to the cementitious matrix during hydration to mitigate autogenous shrinkage [3, 4]. By this method total autogenous shrinkage is reduced and even counteracted in time in cementitious materials made with ordinary Portland cement with or without silica fume [3-8]. Most concrete structures are made with binders containing supplementary cementitious materials (SCMs) like fly ash (FA) or blast-furnace slag (BFS). The influence of the SAPs on the autogenous shrinkage properties of those kinds of materials needs to be studied in detail.

In the literature, only few results of autogenous shrinkage in FA systems can be found. In one study [9] there was 200 $\mu\text{m/m}$ shrinkage strain for a mixture with cement and a water-to-binder ratio of 0.30, 100 $\mu\text{m/m}$ shrinkage strain for FA40 (with 60% of cement and 40% of FA in the binder), 50 $\mu\text{m/m}$ shrinkage strain for FA60, 20 $\mu\text{m/m}$ expansion strain for FA60IC (internal curing) and 60 $\mu\text{m/m}$ expansion strain for FA40IC at an age of 14 days when using lightweight aggregates. In another study [10] for mixtures with a water-to-binder ratio of 0.30, a reference with OPC (at 192 days) showed 320 $\mu\text{m/m}$ shrinkage strain, FA15 (with 85% of cement and 15% of FA in the binder) 250 $\mu\text{m/m}$ shrinkage strain, FA30 220 $\mu\text{m/m}$ shrinkage strain and FA45 150 $\mu\text{m/m}$ shrinkage strain. The cement clinker and SCMs hydrate simultaneously and their reactions are influenced and stimulated by one another. The pozzolanic reaction (by FA) occurs at later time (after a couple of days) as pozzolans need to be activated by the alkaline environment and react with the calcium hydroxide generated by the cement hydration. As the degree of pozzolanic activity increases, the autogenous shrinkage may increase in time. At later ages, the rate of shrinkage is higher in FA mortars compared to pure cement systems. The influence of the internal curing in mixtures containing FA should also be investigated at later ages than 14 days and this data is lacking in the literature. Data from 14 days onwards would be very useful as the net overall shrinkage for FA systems may then exceed the one for the pure cement mixtures.

Next to FA, BFS was also point of interest in terms of autogenous shrinkage. According to the literature, the amount of autogenous shrinkage is higher compared to ordinary Portland systems [11, 12]. There was 310 $\mu\text{m/m}$ shrinkage strain for a cement mixture with a water-to-binder ratio of 0.32, 380 $\mu\text{m/m}$ shrinkage strain for BFS30 (70% of cement and 30% of BFS with a water-to-binder ratio of 0.32) and 420 $\mu\text{m/m}$ shrinkage strain for BFS50 at an age of 200 days. The higher autogenous shrinkage could be due to the denser structure with smaller pores of the BFS cement paste. The smaller pores lead to higher capillary forces, thus increases autogenous shrinkage. A single study investigating internal curing showed that for blast-furnace-slag-blended cement mixtures, part of the autogenous shrinkage was eliminated due to internal curing, but the remaining shrinkage was very high [13]. The shrinkage was

approximately 1400 $\mu\text{m/m}$ shrinkage strain for BFSC-REF (BFS blended cement mixture), 600 $\mu\text{m/m}$ shrinkage strain for BFSC-SAP (mixture with BFS and internal curing), 200 $\mu\text{m/m}$ shrinkage strain for OPC-REF (ordinary Portland cement mixture) and 50 $\mu\text{m/m}$ shrinkage strain for OPC-SAP at an age of 7 days. Results from 7 days onwards are missing in the literature.

In this study, the effects of SAPs in FA and BFS blended mixtures were studied by monitoring the autogenous strain in time, up to one month.

2. Materials and Methods

2.1 Materials

A cement paste with a water-to-binder ratio (W/B) of 0.3 was used as a reference (R0.30). The cement was CEM I 52.5 N and FA and BFS were incorporated to additionally form manually blended cements. The chemical composition and the specific surface area of the used materials can be found in Table 1.

Table 1: Chemical composition of CEM I 52.5 N, Class F FA and BFS [mass-%] and specific surface (Blaine fineness).

	CEM I 52.5 N mass-%	Class F FA mass-%	BFS mass-%
CaO	63.12	2.47	40.38
SiO ₂	18.73	49.34	34.35
Al ₂ O ₃	4.94	24.55	11.36
Fe ₂ O ₃	3.99	6.23	0.48
SO ₃	3.07	0.30	1.65
MgO	1.02	1.73	7.57
K ₂ O	0.77	3.84	0.37
Na ₂ O	0.41	0.52	0.29
Cl ⁻	-	-	0.013
S ²⁻	-	-	0.77
Mn	-	-	0.165
Specific surface	390 m ² kg ⁻¹	330 m ² kg ⁻¹	400 m ² kg ⁻¹

The studied mixtures, all with a W/B=0.30, are the following (together with their percent replacement of the cement): FA15, FA30, FA50, BFS15, BFS30, BFS50 and BFS85. The mixtures were mixed according to the Standard EN 196-1 and were uniformly and homogenously mixed. The dosage of the superplasticizer was kept constant at an amount of 0.42 mass-% (by binder weight) polycarboxylate superplasticizer (Glenium 51, conc. 35%, BASF).

In systems with a water-to-cement ratio of 0.3 complete hydration is not possible. With an additional (entrained) water-to-cement ratio of 0.054 through pre-described water-filled SAP inclusions ((W/B)_c=0.054), internal curing takes over and the self-desiccation is mitigated

[3, 14]. The amount of mixing water absorbed by the SAP was determined in previous research [15, 16]. The amount of SAP to be added to receive an additional entrained water amount of $(W/B)_e=0.054$ was 0.22 mass-% (by binder weight) SAP. SAPs were added in addition (subscript in mixtures _SAP), as well as the additional water needed to induce internal curing, i.e. the SAP absorbed its water from the mix water. The SAP used in this research is a crosslinked copolymer of acrylamide and sodium acrylate (particle size $100.0 \pm 21.5 \mu\text{m}$), produced by bulk polymerization.

2.2 Methods

To determine time-zero to visualize the autogenous strain in time, the Vicat needle test according to the Standard ASTM C191-08 was used in triplicate.

To measure the autogenous strain, the Standard ASTM C1698-09 was followed. In this test, corrugated tubes with a length of $420 \pm 5 \text{ mm}$ and a diameter of $29 \pm 0.5 \text{ mm}$ were used. The length of the specimen was monitored either by means of a manually operated dilatometer or by means of an automated system where the dilatometers with samples were submerged in a polyalkylene-glycol thermobath, as can be seen in Figure 1. All automated measurements were done during temperature control at $20.0 \pm 0.1^\circ\text{C}$. The temperature gradients in the specimens were acceptable [17].

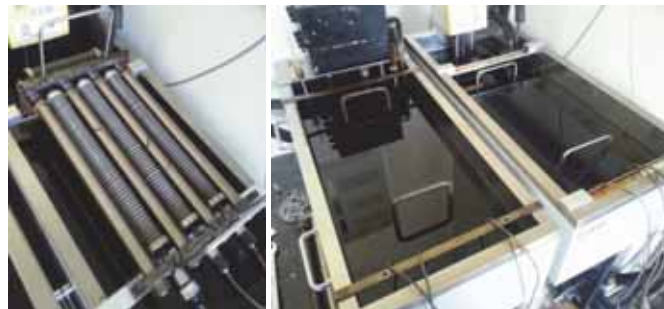
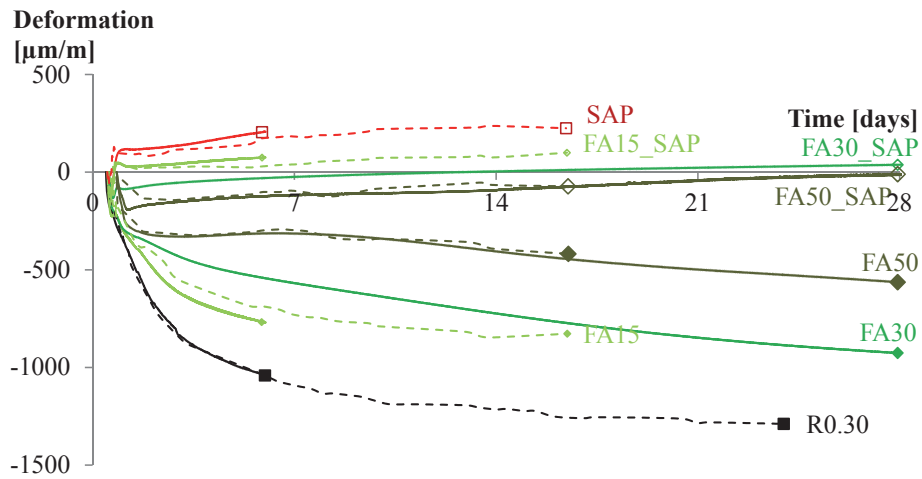


Figure 1: Specimens (left) used for the automated autogenous shrinkage tests (right).

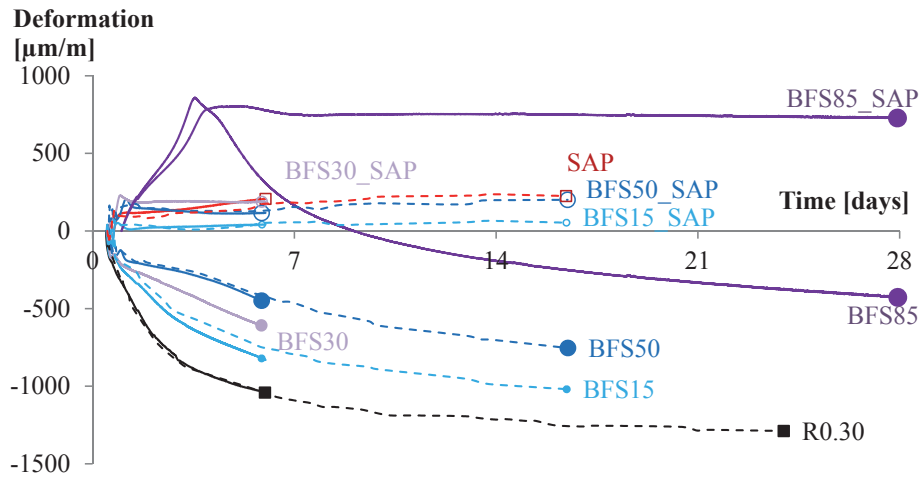
3. Results and discussion

Figure 2 shows the autogenous shrinkage of the specimens over time. The starting point of the curves is final setting time. This was determined by means of the Vicat needle test. The pozzolanic reaction occurs at late ages due to the consumption of or activation by calcium hydroxide and other alkaline components originating from the cement. This caused the setting of systems with higher amounts of FA to occur later in time. The position of the autogenous shrinkage curves is highly influenced by the accuracy of the measured time of final set as the rate of shrinkage is very high around this initial point. Furthermore, comparing the manual

discontinuous tests (dashed lines) with the automated continuous tests (solid lines), it is clear that the data corresponds well. In this way, the effects on the long term (between 7 and 28 days) could be studied and compared by both techniques [17].



(a)



(b)

Figure 2: Autogenous strain $[\mu\text{m/m}]$ for cement paste mixtures with and without FA (a), with and without BFS (b), and with and without entrained water by superabsorbent polymers over 28 days. (--- = manual test curves; — = automated test curves)

The reference mixture with a water-to-binder ratio of 0.30 (R0.30) shows prominent shrinkage. This is due to the fine porosity formed in mixtures with a lower water-to-binder ratio, increasing the hydrostatic tension forces (capillary forces) and leading to the increase in self-desiccation and autogenous shrinkage. In time, the rate of autogenous shrinkage decreases as most of the hydration products have been formed. At 21 days, autogenous shrinkage has almost stopped completely.

The same mixture, but with SAPs added together with additional water (for SAP absorption during mixing), does not show this high-rate shrinkage. Just after setting, there is even a small expansion. This can be caused by several different mechanisms including crystallization pressure of calcium hydroxide [18]. The effect was not prominent and no bleeding occurred in this study. The mixture with $(W/B)_e=0.054$ and SAP seems to mitigate autogenous shrinkage completely at this age, proving the compatibility of the used SAP with the mechanism of internal curing and the usefulness of the application of superabsorbent polymers to mitigate autogenous shrinkage in systems with ordinary Portland cement.

In Figure 2a, the FA systems and their shrinkage are shown. The amount of shrinkage is less in FA systems due to the lower amount of cement at early age, as the initial reaction rate and water consumption is lower. This leads to less autogenous shrinkage at early ages. Only after a couple of days, the pozzolanic reaction takes place, consuming the calcium hydroxide from the cement hydration reaction, increasing the autogenous shrinkage. This can be seen as the sudden increase in slope - or rate of the shrinkage curve - in time. The shift in slope occurs around 8 days and the increase in shrinkage is clearly seen as the curve is shifted downwards. This corresponds to the time where calcium hydroxide started to be depleted due to the pozzolanic reaction [19, 20]. In literature, the same trends at early age are found [10], but shrinkage is mostly monitored till seven days. If one would also do this with these obtained results, one would conclude that the shrinkage would come to a hold at the end of the test (FA50). That is why it is very important to study the effect for a longer time span, for example for one month. Long-term reactions, such as the pozzolanic reaction, influence the autogenous shrinkage properties at these later ages. If the amount of FA is high, i.e. 50% (FA50), the reaction degree of the FA decreases due to an insufficient amount of $\text{Ca}(\text{OH})_2$ formed during cement hydration [19]. At higher FA contents the FA would only function as a filler component.

In systems with FA and internal curing ($_SAP$), the autogenous shrinkage is mitigated (Figure 2a). Generally, superabsorbent polymers are able to mitigate autogenous shrinkage in FA systems with a low water-to-binder ratio.

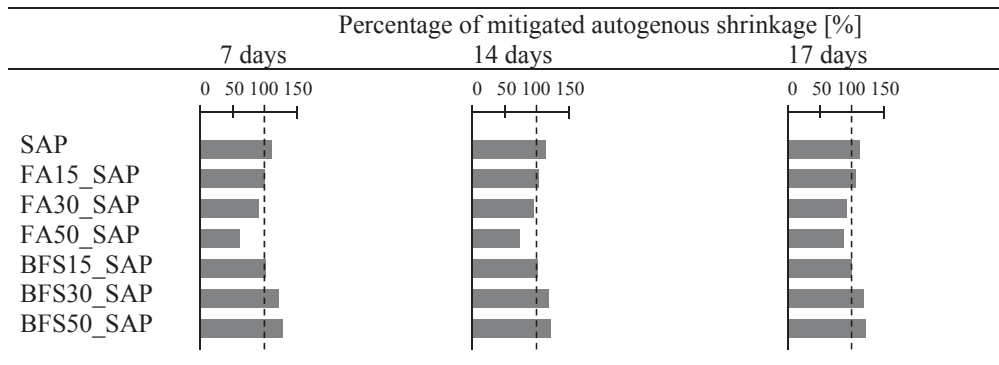
In Figure 2b, the shrinkage results for the latent-hydraulic BFS mixtures can be found. It is a slow reacting material, leading to less strain at early ages. After 5 days, the rate of autogenous shrinkage is higher as the slag reaction takes place. On one hand, the microstructure in BFS systems should be denser and the pores smaller, which should lead to higher capillary forces, self-desiccation and autogenous shrinkage. On the other hand, the slag reaction occurs at later ages, thus the densification of the cementitious matrix would occur also at later ages. That is why the shrinkage is lower at early age. The level for maximum reaction degree of BFS in blended cement is approximately 60-70% [21], so in BFS85 not all BFS is used and it will act

as filler as well. There is almost no shrinkage in BFS85 mixtures at early age, due to the low calcium hydroxide amount from the hydraulic reaction of the cement. There is even a vast expansion at early age. In time there is a prominent shrinkage due to the slow latent hydraulic reaction of BFS. Re-absorption of bleeding water may also generate expansion, but bleeding was not clearly observed in any of the specimens. It could also be that the early-age expansion resulted from the later-occurring heat of hydration.

When using SAPs in BFS mixtures, autogenous shrinkage is again mitigated for all studied specimens. This shows the potential of SAPs for mitigating autogenous shrinkage in pure cement, FA and BFS blended cement systems. The ion concentration in the pore fluid is also different and the swelling capacity of the SAPs with mixing water may be expected to be different between the mixtures. This would lead to different internal curing amounts. Here, however, no differences were found in flow characteristics and macro porosity [15] between the different mixtures indicating that the absorption of pore fluids was the same in all mixtures.

The percentage of mitigated autogenous shrinkage for the different mixtures is shown in Table 2. The percentage was calculated as the autogenous shrinkage of a specimen without SAP at a specific age minus the shrinkage in a SAP specimen with the same matrix and age over the strain in the specimen without SAPs. A percentage of more than 100% indicates an expansion, and thus the shrinkage was completely compensated by the SAP.

Table 2: The percentage of mitigated autogenous shrinkage [%] over time.



* The values for BFS85_SAP are not given as they are off scale, but similar shrinkage mitigation for this mixture is evident from Figure 2.

Again, in all systems with SAPs, there is mitigation of autogenous shrinkage in time. The values over time are also comparable, demonstrating SAPs as good means of mitigation in time due to release of mixing water towards the cementitious matrix.

The results in this paper are for manually blended cement compositions (with FA or BFS). Commercially available cement types such as CEM II-III-IV-V are expected to follow the

same trend, but other initial constituents may be present. This may have an effect on the autogenous shrinkage properties.

4. Conclusions

- Irrespective to the mixture, both the manual and automated tests show the same trend and quantitative values. In this way, all obtained results are comparable.
- In both fly ash and blast-furnace slag systems, where part of the cement is replaced by SCMs, the initial total amount of autogenous shrinkage is lower compared to an ordinary Portland cement mixture with a water-to-binder ratio of 0.30.
- At later ages, the rate of autogenous shrinkage is higher compared to ordinary Portland cement mixtures. It is therefore important to study the effects of autogenous shrinkage on the long term, rather than stopping at an age of 7 days.
- Internal curing by means of superabsorbent polymers can be successfully applied independent of this long-term higher rate of shrinkage in mixtures with supplementary cementitious materials.
- Superabsorbent polymers are able to mitigate autogenous shrinkage in mixtures with a water-to-binder ratio of 0.30, with or without fly ash and/or blast-furnace slag as a supplementary cementitious material.

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